

DETERMINATION OF CHONDRULE COOLING RATES FROM TRACE ELEMENTS REVISITED. C. M. O'D. Alexander and J. Wang. Dept. of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. N.W., Washington DC 20015, U.S.A..

Introduction. The cooling rates of chondrules not only provide important information on the physical environment in which chondrules formed but also help constrain, through modeling and experiment, the influence that processes, such as evaporation, may have had on bulk chondrule compositions. Cooling rates for porphyritic chondrules have been estimated by comparing either the textures or minor element zoning patterns in natural and synthetic chondrules [e.g. 1, 2, 3]. Both approaches suggest chondrules formed at cooling rates of between 100°C/hr and 1000°C/hr. Previous estimates of cooling rates based on trace element abundances in chondrule phenocrysts favored cooling rates of 1000°C/hr or higher [4], but a more recent study suggests that at least some chondrules formed at intermediate cooling rates between about 100°C/hr and 1000°C/hr [5]. Here we present the initial results of a re-examination of cooling rate estimates based on trace element abundances using the improved sensitivity of the Carnegie's new Cameca 6f ion microprobe. Our results are similar to those of [4], suggesting cooling rates 1000°C/hr but some ambiguities remain.

Kennedy et al. (1993) showed that the distribution coefficients of highly incompatible trace elements in olivine and low-Ca pyroxene are a function of cooling rate at rates greater than ~100°C/hr. Three of the most cooling rate sensitive trace elements are Ba, La and Ce. For instance, at a cooling rate of about 2196°C/hr, their distribution coefficients increase by up to a factor of 1000 compared to those at cooling rates of less than 100°C/hr.

However, determining the distribution coefficients of these elements in chondrules is complicated by the fact that the composition of the liquid from which the crystals grew is not well constrained. In porphyritic chondrules, the phenocrysts are the dominant component, so that during crystallization the composition of the residual liquid will change considerably. Most chondrules have nearly chondritic bulk compositions and were largely molten at the onset of crystallization, but by the time crystallization ceased incompatible element abundances in chondrule mesostases, the residual melts, are typically 5-15 times OC [4]. The relative abundances of most refractory elements in bulk chondrules, including Ba and the REEs, are essentially chondritic. Since even at high cooling rates the distribution coefficients of all these elements are low, their relative abundances will not change much during crystallization. The distribution coefficients of the two most compatible REEs, Yb and Lu ($D \approx 0.02$), are only slightly affected by cooling rate [6]. Therefore, their abundances in the phenocrysts should reflect the degree of enrichment of REEs in the melt from which the grains are growing. Thus, ratioing

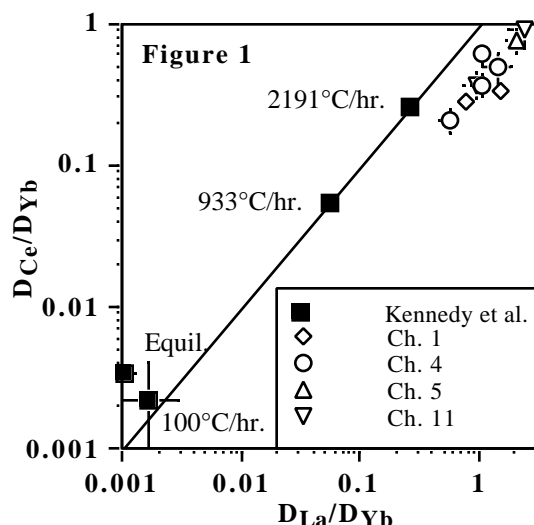
the Ba, La and Ce abundances to those of Yb or Lu and normalizing these to the chondritic ratios should provide one with a measure of their relative distribution coefficients, which is cooling rate sensitive but independent of the degree of crystallization.

Using this approach, [4] concluded, on the basis of (La, Ce)/Lu ratios determined by ion microprobe, that both porphyritic olivine and pyroxene chondrules formed at cooling rates of ~1000°C/hr or higher. On the other hand, [5] concluded, also from REE data, that four porphyritic pyroxene chondrules they examined formed at cooling rates that were greater than 100°C/hr but significantly less than 1000°C/hr. Given the importance of cooling rate to our understanding of the genesis of chondrules, we have undertaken to re-examine the use of distribution coefficients to estimate cooling rates utilizing the improved sensitivity of the Carnegie's new Cameca 6f ion microprobe. In particular, we have concentrated on the (Ba, La, Ce)/(Yb, Lu) system, as well as the independent but also cooling rate sensitive system (Zr, Nb)/Al.

Experimental. Trace element analyses were carried out with a 12.5kV O⁻ primary beam, 10kV secondary accelerating voltage, a 50eV energy window and -75V energy offset. The typical primary beam current was ~10nA and a typical spot size was about 25-30mm. Background count rates were monitored during all analyses at mass 130.5. The results for all masses were always significantly above this background. Molecular interferences were corrected for using the procedures outlined by [4, 7]. There are no well determined olivine standards for the elements of interest here. However, the influence of the matrix on trace element sensitivity factors in silicates is small. The sensitivity factors for La, Ce, Yb and Lu were determined from four basaltic glasses previously analyzed by isotope dilution. The results from all four glasses are within 10% of one another. La and Ce sensitivity factors determined from the NBS 610 standard glass using the abundances determined by [8] are within 3% of the mean obtained from the basaltic glasses. The Ba abundance was measured by isotope dilution in one of the basaltic glasses and by INAA in another, and the sensitivity factors for Ba determined from them agree within 5%. The Al sensitivity factor was determined from the four basaltic glasses, as well as the NBS 610 and 612 standard glasses, and all agree to within 5%. Nb and Zr sensitivity factors are the most poorly determined. Zr has been determined in two of the basaltic glasses but their sensitivity factors differ by 30%. The Nb abundance is only known for one of the glasses but based on the results for the other elements it is unlikely to be in error by more than 30%.

Results. To date, we have reanalyzed olivine phenocrysts from four Bishunpur porphyritic olivine

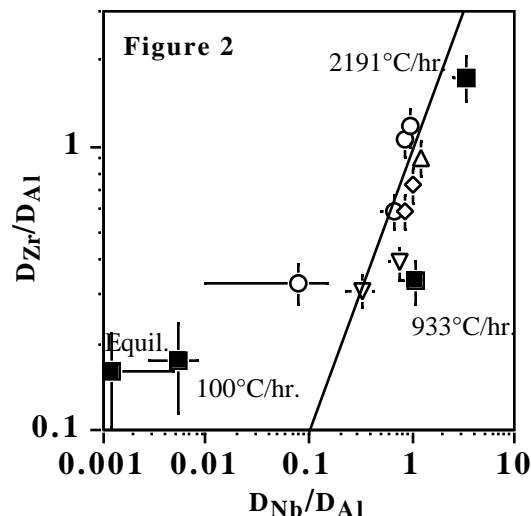
chondrules (B1, B4, B5 and B11) studied by [4]. The measured trace element abundances are generally very similar to those found by [4], but the precision is considerably improved. Figures 1 and 2 summarize the results obtained for the cooling rate sensitive systems.



The REE abundance patterns, normalized to bulk OC, are relatively flat in all four chondrules but increase at Yb and Lu, consistent with the fast cooling rate experiments of [6]. What was not anticipated from the experiments of [6], is that the chondrite normalized abundances of La (and Ba) in the chondrule phenocrysts are enhanced compared to Ce and other LREEs, by factors of 2-5. In Figure 1, the experimental results lie along a slope 1 line, consistent with La (and Ba) and Ce being incorporated into the olivine without significant relative fractionation during crystallization. The chondrule data parallel this line but are offset to higher La/Yb (and Ba/Yb) ratios. These enrichments are much larger than can be explained by the errors in the analyses or uncertainties in the sensitivity factors. A similar enhancement was seen by [4], particularly for the more precisely determined refractory-rich olivines.

The enhanced La and Ba abundances are unlikely to be due to unrecognized interferences or to changes in the sensitivity factors of these two elements at the low concentrations present in chondrule olivines. They may either reflect higher distribution coefficients in the natural chondrules or incorporation of small glass inclusions with super chondritic (La,Ba)/Yb ratios. Incorporation of glass inclusions in the analyses is the single largest potential source of error because the glass is highly enriched in the same incompatible elements being used to determine cooling rates. [6] showed that incorporation of only 0.7wt% of melt in an olivine grain that formed at low cooling rates would produce a composition similar to those of crystals formed at 2000°C/hr. However, no inclusions were observed in the areas analyzed. Also, most porphyritic olivine chondrule glasses have La/Yb ratios that are

within 20-30% of chondritic. The same is true for Ba/Yb ratios in glasses, though some are depleted by up to a factor of ~2. Nevertheless, since smaller spots are less likely to incorporate glass inclusions, in the future we will analyze these and other chondrules with smaller, focused spots.



The (Zr,Nb)/Al results (Fig. 2) are also consistent with formation at high cooling rates. Although most of the data lie between the 933°C/hr and 2191°C/hr experimental points, unlike the (Ba,La,Ce)/Yb data which are at or above the 2191°C/hr data points. The difference in behavior is somewhat surprising since Nb is, if anything, less compatible and more cooling rate sensitive than Ba, La or Ce. Hence, if incorporation of inclusions is the explanation for the high (Ba,La,Ce)/Yb ratios, one might expect to see a similar degree of enrichment in Nb.

Conclusions. The preliminary results reported here are similar to those previously obtained by [4] and suggest that cooling rates during formation of the chondrules analyzed were in excess of 1000°C/hr. However, there are significant differences in the apparent distribution coefficients for Ba and La between synthetic and natural chondrules, and between cooling rates estimated from (Ba,La,Ce)/Yb and (Zr,Nb)/Al ratios. At present, it cannot be excluded that small melt inclusions in the analyzed areas have led to overestimates of the cooling rates. Consequently, the conclusion that chondrules formed at cooling rates in excess of 1000°C/hr remains tentative.

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